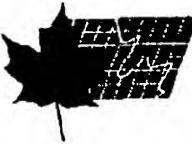


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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Process for Preparing Formylcarboxylic Esters

(72) Bahrmann, Helmut - Germany (Federal Republic of) ;
Lappe, Peter - Germany (Federal Republic of) ;
Feil, Bernhard - Germany (Federal Republic of) ;
Leckel, Dieter - Germany (Federal Republic of) ;
Schobben, Christian - Germany (Federal Republic of) ;

(71) Hoechst Aktiengesellschaft - Germany (Federal Republic
of) ;

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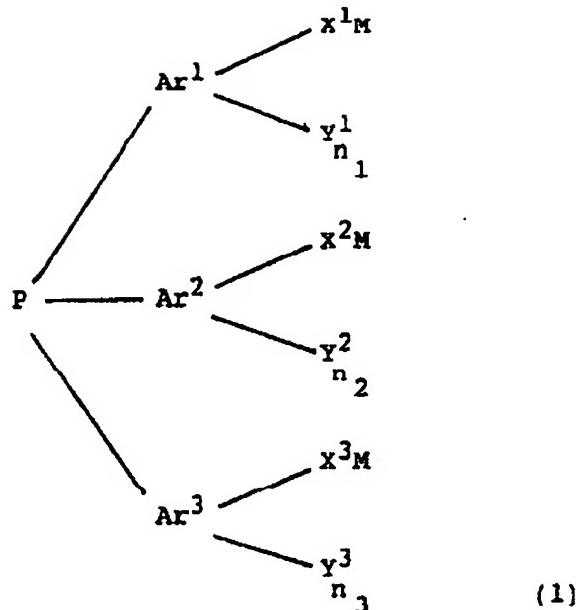
Hoechst Aktiengesellschaft, 65926 Frankfurt am Main

Abstract

A process is described for preparing di- and polyformyl-carboxylic esters by hydroformylation of esters of multiply unsaturated fatty acids. The reaction is carried out in the presence of an aqueous solution containing rhodium carbonyl/phosphine complexes as catalyst and additionally a surfactant.

Patent claims

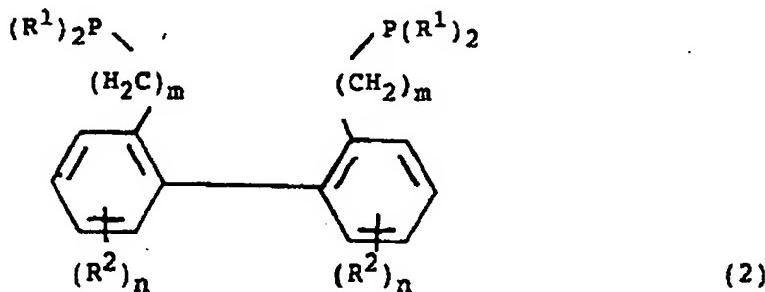
1. A process for preparing di- and polyformylcarboxylic esters, which comprises reacting esters of multiply unsaturated fatty acids and low molecular weight monoalcohols with carbon monoxide and hydrogen at from 100 to 180°C and from 5 to 35 MPa in the presence of an aqueous solution containing rhodium-phosphine complexes as catalysts and additionally a solubilizer.
- 10 2. The process as claimed in claim 1, wherein the fatty acids are doubly or triply unsaturated and contain from 8 to 25 carbon atoms in the molecule.
- 15 3. The process as claimed in claim 1 or 2, wherein the unsaturated fatty acids contain from 10 to 20 carbon atoms in the molecule.
4. The process as claimed in one or more of claims 1 to 3, wherein the low molecular weight monoalcohols are saturated and contain from 1 to 10 carbon atoms in the molecule.
- 20 5. The process as claimed in one or more of claims 1 to 4, wherein the monoalcohol is methanol.
6. The process as claimed in one or more of claims 1 to 5, wherein the phosphine is a monophosphine of the formula



where Ar^1 , Ar^2 , Ar^3 are each a phenyl or naphthyl group, y^1 , y^2 , y^3 are each a straight-chain or branched alkyl group having from 1 to 4 carbon atoms, an alkoxy group, a halogen atom, the OH, CN, NO₂, or R¹R²-N groups, where R¹ and R² are each a straight-chain or branched alkyl group having from 1 to 4 carbon atoms; X¹, X², X³ are each a sulfonate (SO₃⁻) or carboxylate (COO⁻) radical, n₁, n₂, n₃ are identical or different integers from 0 to 5. M is an alkali metal ion, one chemical equivalent of an alkaline earth metal or zinc ion, an ammonium or quaternary ammonium ion of the formula N(R³R⁴R⁵R⁶)⁺, where R³, R⁴, R⁵, R⁶ are each a straight-chain or branched alkyl group having from 1 to 4 carbon atoms.

7. The process as claimed in one or more of claims 1 to 5, wherein monophosphines used are the reaction products of dialkylphosphines or diarylphosphines with 1,2-, 1,3- or 1,4-butanesultones.

8. The process as claimed in one or more of claims 1 to 5, wherein the phosphines used are diphosphines of the formula



5 where R¹ are identical or different alkyl, cycloalkyl, phenyl, tolyl or naphthyl radicals, R² are identical or different and are hydrogen, alkyl or alkoxy radicals having from 1 to 14 carbon atoms, cycloalkyl, aryl or aroxy radicals having from 6 to 14 carbon atoms or a fused benzene ring, m are identical or different and are integers from 0 to 5 and n are likewise identical or different and are integers from 0 to 4.

10

15 9. The process as claimed in one or more of claims 1 to 8, wherein the surfactants used are cationic surfactants or amphoteric surfactants.

10. The process as claimed in claim 9, wherein the cationic surfactants are tetraalkylammonium salts.

11. The process as claimed in claim 9, wherein the amphoteric surfactants are betaines or amine oxides.

20 12. The process as claimed in one or more of claims 1 to 11, wherein the concentration of the surfactant in the aqueous catalyst solution lies above the critical micelle formation concentration.

2162083

- 16 -

13. The process as claimed in one or more of claims 1 to 12, wherein the reaction is carried out at from 120 to 140°C and from 15 to 20 MPa.
- 5 14. The process as claimed in one or more of claims 1 to 13, wherein the rhodium concentration in the aqueous catalyst solution is from 100 to 600 ppm by weight, preferably from 300 to 400 ppm by weight, based on the solution.
- 10 15. The process as claimed in one or more of claims 1 to 14, wherein at least 20 mol, preferably from 40 to 60 mol, of P(III) in the form of a phosphine are present per mole of rhodium.
- 15 16. The process as claimed in one or more of claims 1 to 15, wherein the pH of the aqueous catalyst solution is at least 3, preferably from 5 to 10 and in particular from 6 to 8.

Fetherstonhaugh & Co.,
Ottawa, Canada
Patent Agents

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Process for preparing formylcarboxylic esters

The invention relates to a process for preparing di- and polyformylcarboxylic esters by hydroformylation of esters of multiply unsaturated fatty acids in the presence of an aqueous solution containing rhodium carbonyl/phosphine complexes as catalyst and additionally a surfactant.

The hydroformylation of unsaturated fatty acid esters is attracting increasing interest. This is based, in particular, on the fact that the starting materials are frequently native raw materials or substances produced from native raw materials which are available in large quantities. The reaction products of the hydroformylation, mono- or polyformylcarboxylic esters, which can also still contain reactive double bonds, are sought-after intermediates. They can be further processed into widely used products such as polyamines, polyurethanes, alkyd resins, plasticizers and synthetic lubricants.

The hydroformylation of higher, multiply olefinically unsaturated compounds has already been repeatedly studied. A problem in this reaction is the high molecular weight of starting material and reaction product, which makes separation and recycling of the catalyst homogeneously dissolved in the reaction product, e.g. by distillation, impossible. Furthermore, when using multiply unsaturated compounds having isolated but closely spaced double bonds, double bond isomerization in the hydroformylation can only be avoided by means of rhodium carbonyl/tertiary phosphine complex catalyst systems.

A problem critical to the economics of the process is the loss-free separation of the homogeneously dissolved catalyst system from the reaction product and its recycling in active form to the hydroformylation reactor. Hitherto, it has only been possible to separate the rhodium/phosphine catalyst from the reaction mixtures containing formyl-fatty acid esters from the hydroformylation of monounsaturated fatty acid esters. However, the

procedure requires complicated measures, furthermore, the catalyst is obtained in inactive form and the phosphine part of the catalyst system is completely lost (J. Amer. Oil Chem. Soc. Vol. 50, 455 (1973)).

5 Linoleic and linolenic methyl esters can be hydroformylated in the presence of heterogenized rhodium carbonyl/phosphine complex catalysts based on polysiloxane (Chemiker-Zeitung, 115 (1991, p. 39 ff)). When using methyl linoleate, the process gives mono- and diformylstearyl esters in yields of up to 95%, based on the doubly unsaturated ester used. Linolenic acid too gives, in the hydroformylation in the presence of the specified catalyst system, only the diformyl compound; in contrast, at most subordinate amounts of trifomyl products are obtained. The rhodium recovery is on average about 0.5% of the noble metal originally used. It cannot be ruled out that a part of the catalyst metal is present in homogeneously dissolved form in equilibrium with the fixed metal, so that the hydroformylation takes place not only over the fixed-bed catalyst, but also in solution.

It is therefore an object of the invention to develop a process which allows esters of unsaturated fatty acids to be hydroformylated, with multiply unsaturated fatty acid esters being not only partially, but completely hydroformylated. In addition, noble metal losses should be largely avoided.

The above-described object is achieved by a process for preparing di- and polyformylcarboxylic esters. It comprises reacting esters of multiply unsaturated fatty acids and low molecular weight monoalcohols with carbon monoxide and hydrogen at from 100 to 180°C and from 5 to 35 MPa in the presence of an aqueous solution containing rhodium-phosphine complexes as catalysts and additionally a surfactant.

35 The hydroformylation of olefins having more than 6 carbon

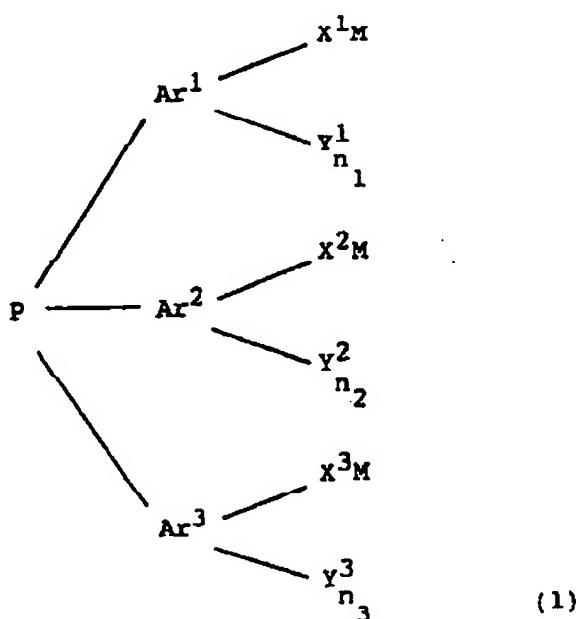
atoms in the molecule in the presence of an aqueous solution containing rhodium complexes as catalyst and additionally a quaternary ammonium salt as solubilizer is known from EP-B-157 316. A further development of this 5 process is subject matter of EP-B-163 234. According to this patent, C₆- to C₂₀-olefins are reacted with hydrogen and carbon monoxide in the presence of rhodium or a sulfonated arylphosphine whose cation is a quaternary ammonium ion.

10 Both processes concern exclusively the reaction of monounsaturated compounds which, in addition, contain no functional groups. Surprisingly, the new process enables a plurality of double bonds present in the ester molecule, including internal double bonds, to be simultaneously hydroformylated, giving, for example, diformyl 15 products from doubly unsaturated compounds and trifomyl products from triply unsaturated compounds.

Starting compounds for the process of the invention are esters whose one component is a multiply, in particular 20 doubly and triply, unsaturated fatty acid having from 8 to 25, preferably from 10 to 20, carbon atoms in the molecule and whose other component is a saturated mono-alcohol having from 1 to 10 carbon atoms in the molecule, 25 preferably methanol. These esters are obtained from natural oils, if desired previously refined and distilled, by transesterification. Examples of natural oils as basis of the acid component of the starting ester are cottonseed oil, thistle oil, peanut oil, pumpkin kernel oil, linseed oil, corn oil, soybean oil and sunflower 30 oil.

Catalysts used in the process claimed are rhodium compounds containing coordinated water-soluble phosphines, i.e. salts whose anion is a phosphine which contains at least one sulfonated or carboxylated aromatic radical. 35 The term phosphine also includes those compounds of trivalent phosphorus in which the phosphorus atom is a

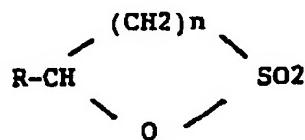
constituent of a heterocyclic ring. The aromatic radical can be bonded to the phosphorus atom of the phosphine either directly or via other groups. Examples of aromatic radicals are the phenyl and the naphthyl radical. They 5 can be singly or multiply sulfonated or carboxylated and in addition can be substituted by further atom groups or atoms such as alkyl, hydroxyl, halide. Monophosphine anions are preferably derived from compounds of the formula (1)



10 Here, Ar^1 , Ar^2 , Ar^3 are each a phenyl or naphthyl group, Y^1 , Y^2 , Y^3 are each a straight-chain or branched alkyl group having from 1 to 4 carbon atoms, an alkoxy group, a halogen atom, the OH, CN, NO, or R^1R^2-N groups, where R^1 and R^2 are each a straight-chain or branched alkyl group 15 having from 1 to 4 carbon atoms; X^1 , X^2 , X^3 are each a sulfonate (SO_3^-) or carboxylate (COO^-) radical, n_1 , n_2 , n_3 are identical or different integers from 0 to 5. M is an alkali metal ion, one chemical equivalent of an alkaline earth metal or zinc ion, an ammonium or quaternary 20 ammonium ion of the formula $N(R^3R^4R^5R^6)^+$, where R^3 , R^4 , R^5 , R^6 are each a straight-chain or branched alkyl group having from 1 to 4 carbon atoms.

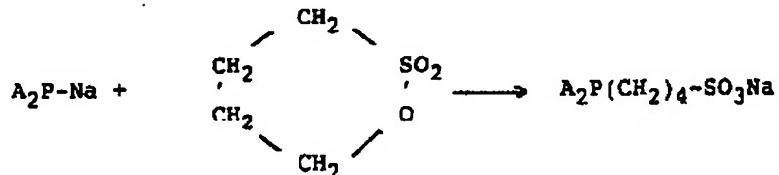
Preference is given to compounds of the above-described formula in which Ar^1 , Ar^2 , Ar^3 are each a phenyl radical and X^1 , X^2 , X^3 are each a sulfonate radical in the meta position to the phosphorus (tris(*m*-sulfonatophenyl)phosphine, abbreviated as TPPTS).

A further group of monophosphines suitable as catalyst component are obtained by sulfalkylation of dialkylphosphines or diarylphosphines containing 1,2-, 1,3- or 1,4-sultones



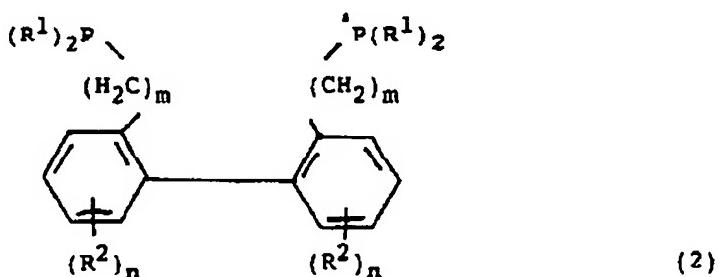
10 (where n = 0, 1 or 2 and R = H, alkyl).

e.g. corresponding to



where A are identical or different alkyl or aryl radicals.

The anion can be formed not only from monophosphines but 15 also from polyphosphines, in particular diphosphines, which contain at least one sulfonated or carboxylated aromatic radical. Diphosphine anions are preferably derived from diaryl compounds of the formula (2)



which are substituted by at least one sulfonate (SO_3^-) radical or carboxylate (COO^-) radical. In the formula, R^1 are identical or different alkyl, cycloalkyl, phenyl, tolyl or naphthyl radicals, R^2 are identical or different and are hydrogen, alkyl or alkoxy radicals having from 1 to 14 carbon atoms, also cycloalkyl, aryl or aroxy radicals having from 6 to 14 carbon atoms or a fused benzene ring, m are identical or different and are integers from 0 to 5 and n are likewise identical or different and are integers from 0 to 4. Preference is given to the sulfonated compounds which are obtainable by conventional methods. Useful representatives of this class of compounds are the products obtained by sulfonation of 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl or 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthyl. An example which may be mentioned of the anion of a heterocyclic phosphorus compound is 3,4-dimethyl-2,5,6-tris(p-sulfonatophenyl)-1-phosphanorbornadiene.

The alkali metal salts or the ammonium salts, in particular the sodium salts, of the sulfonated or carboxylated phosphines are usually used as catalyst constituent.

An essential feature of the new method is the addition of a surfactant (also described as solubilizer, phase-transfer, surface-active or amphiphilic reagent) to the aqueous catalyst solution. For the purposes of the present invention, surfactants are substances or mixtures

- of substances which are compatible both with the aqueous phase (the catalyst) and with the organic phase (the unsaturated fatty acid ester) and are soluble in both phases, at least at elevated temperatures. The task of 5 the surfactants is improving the solubility of the fatty acid ester in the catalyst solution. This occurs by aggregation of the surfactant particles to form micelles above the critical micelle formation concentration (c.m.c., cf. Ullmanns Encyclopädie der technischen 10 Chemie, 4th edition, 1982, volume 22, pages 464, 465) characteristic of each surfactant. The ester molecules accumulate in the micelles and are transported in this form into the aqueous catalyst phase in which the reaction with the synthesis gas occurs.
- 15 According to the chemical structure, distinctions are made between anionic surfactants such as the soaps, alkyl sulfates, alkylbenzenesulfonates and alkylbenzene phosphates, cationic surfactants whose most important representatives are the tetraalkylammonium salts, amphoteric 20 surfactants containing zwitterionic hydrophilic groups and of which the aminocarboxylic acids, betaines, sulfobetaines and amine oxides are examples and finally non-ionic surfactants which include alkyl and alkylphenyl polyethylene glycol ethers, fatty acid alkyloamides and 25 sucrose fatty acid esters.

In the process of the invention, preference is given to using amphoteric surfactants and, in particular, cationic surfactants, e.g. tetrahexylammonium bromide, tetradecylammonium bromide, N-dodecyl-N,N,N-trimethylammonium bromide, N-tetradecyl-N,N,N-trimethylammonium bromide, N-hexadecyl-N,N,N-trimethylammonium bromide, N-octadecyl-N,N,N-trimethylammonium bromide and amphoteric surfactants such as N,N-dimethyldodecylammonium betaine, N,N-dimethyloctylamine N-oxide, N,N-dimethyldecylamine N-oxide, N,N-dimethyldodecylamine N-oxide, N,N-dimethyltetradecylamine N-oxide. The surfactants can be used as uniform substances or as mixtures. The concentration of 30 35

- 8 - 2162083

the surfactant in the aqueous catalyst solution lies above the critical micelle formation concentration under the reaction conditions of the hydroformylation reaction.

5 The reaction of the multiply unsaturated fatty acid ester with hydrogen and carbon monoxide is carried out at temperatures of from 100 to 180°C, in particular from 120 to 140°C, and pressures of from 5 to 35 MPa, preferably from 15 to 20 MPa.

10 The catalyst can be added to the reaction system in a preformed stack. However, it can be prepared with equally good results from the components rhodium or rhodium compound and the aqueous solution of the sulfonated or carboxylated phosphine under the reaction conditions in the reaction mixture, i.e. in the presence of the fatty acid ester. Apart from metallic rhodium in finely divided form, the rhodium source used can be water-soluble rhodium salts such as rhodium chloride, rhodium sulfate, rhodium acetate or compounds soluble in organic media such as rhodium 2-ethylhexanoate or insoluble compounds 15 such as rhodium oxides.

20 The rhodium concentration of the aqueous catalyst solution is from 100 to 600 ppm by weight, preferably from 300 to 400 ppm by weight, based on the solution. To rule out isomerization of the unsaturated fatty acid ester, 25 the sulfonated or carboxylated phosphine is used in such an amount that at least 20 mol, preferably from 40 to 80 mol, of P(III) are present per mole of rhodium.

30 The pH of the aqueous catalyst solution should not be below a value of 3. In general, the pH is set to from 5 to 10, preferably from 6 to 8.

The composition of the synthesis gas, i.e. the ratio of carbon monoxide to hydrogen, can be varied within wide limits. In general, the synthesis gas used is one in which the volume ratio of carbon monoxide to hydrogen is

1 : 1 or deviates only little from this value.

The reaction can be carried out either batchwise or continuously.

5 The process of the invention is illustrated by the following examples, but is not restricted to the embodiments presented.

Experimental procedure

For the synthesis of the diformyl and triformyl derivatives of fatty acid methyl esters by hydroformylation of 10 multiply unsaturated fatty acid methyl esters, use was made either of technical-grade linseed oil fatty acid methyl ester mixture having a composition of 55% of methyl linolenate, 15% of methyl linoleate and 20% of methyl oleate, remainder saturated fatty acid methyl esters, or a mixture consisting of 90% of methyl linolenate and 10% of methyl linoleate. The reactions 15 were carried out in 160 ml V4A steel autoclaves having a pressure-resistant dropping funnel, pressure sensor, bursting disk and thermocouple. A magnetically coupled propeller stirrer having holes for introducing gas 20 provides intensive mixing of the reaction mixture.

The catalyst solution was prepared in a Schlenk tube flushed with argon which was charged with the calculated amounts of rhodium compound ($\text{Rh}_4(\text{CO})_{12}$, $\text{HRh}(\text{CO})_4\text{NaTPPTS}$), 25 or $\text{Rh}_2(\text{SO}_4)_3$, phosphine ligand, oxygen-free water and surfactant. The pH of the catalyst solution was set using NaHCO_3 , or alkali metal hydroxide.

To prepare the actual hydroformylation catalyst, the catalyst solution was pretreated with synthesis gas for 30 one hour while stirring and under the temperature and pressure conditions of the hydroformylation in an autoclave which had been flushed with argon and then with synthesis gas. Subsequently, the unsaturated ester was

added dropwise.

The fall in pressure could be monitored during the reaction using a pressure sensor with associated recorder. After the reaction was complete, the autoclave
5 was cooled, slowly vented and the reaction mixture was transferred to a separating funnel. Aqueous and organic phases were separated, the organic phase was taken up in ether and washed twice with twice its amount of distilled water. While presumably little rhodium goes into the
10 organic phase, the latter was additionally washed with NaTPPTS solution. The organic phase was dried over Na_2SO_4 , filtered, the ether was distilled off and the hydroformylation product was analysed.

15 The hydrogenation of the hydroformylation product to give the corresponding hydroxymethyl compounds was carried out at 100°C and 14 MPa H₂ pressure using, as catalyst, 10% by weight (based on the hydroformylation product) of Raney nickel slurry in methanol. As solvent, the same volume of methanol was used. The reaction product freed
20 of catalyst by filtration and of methanol by distillation was characterized by its fat-chemical parameters (iodine number, carbonyl number, hydroxyl number).

Example 1

A 160 ml magnetically stirred autoclave was charged with
25 10 g of technical-grade linseed oil fatty acid ester mixture (ester mixture based on the catalyst phase) together with 20 cm³ of an aqueous catalyst solution containing 0.08 mmol (200 ppm by weight) of Rh, 1.6 mmol of NaTPPTS (P/Rh ratio 20), 3.2 mmol of tetradecyltrimethylammonium bromide (7.5 times c.m.c.) and had been
30 adjusted to a pH of 8 using Na_2CO_3 . The two liquid phases and the gas phase were intensively mixed at a reaction pressure of 20 MPa and a temperature of 120°C. After a reaction time of 12 hours, the autoclave was cooled,
35 vented and the reaction product was worked up as

described above. The conversion was 100%. The reaction product had a composition of 26% by weight of monoformyl product, based on the ester mixture used, 30% by weight of diformyl product, based on the methyl linoleate and 5 methyl linolenate contents of the ester mixture, and 47% by weight of trishydroformylation products, based only on the methyl linolenate content of the ester mixture. The above method of calculating the yield was also employed for all other experiments using the technical-grade 10 linseed oil fatty acid methyl ester mixture.

Examples 2 - 6

Technical-grade linseed oil fatty acid methyl ester mixture was hydroformylated in the presence of the water-soluble rhodium carbonyl/NaTPPTS catalyst system as 15 described in Example 1, but with variation of the surfactant. The results are summarized in Table 1.

Table 1

	Surfactant	pH of cat. sol.	MF	DF	TF	Conversion	
						% by weight]
	Ex. 2 $[(C_{16}H_{33}N^+(CH_3)_2)_2]Br^-$	8	30	33	42	94	
	Ex. 3 $[(C_{18}H_{37}N^+(CH_3)_2)_2]Br^-$	8	29	44	40	100	
20	Ex. 4 $[(C_{12}H_{25}N^+(CH_3)_2)_2]Br^-$	8	33	26	29	96	
	Ex. 5 $C_{14}H_{29}(CH_3)_2N^-O^-$	5.6	32	41	38	99	
	Ex. 6 $[C_{12}H_{25}(CH_3)_2N^+]^-COO^-CH_2-$	5.6	39	17	5	78	

(MF, DF, TF = monoformyl, diformyl, triformal products)

Example 7

25 Technical-grade linseed oil fatty acid ester mixture was hydroformylated as described in Example 1, but using three times the rhodium concentration (600 ppm of rhodium) and twice the P/Rh ratio (40 : 1). The conversion was quantitative. The product mixture contained:

27% by weight of monoformyl products

30% by weight of diformyl products

52% by weight of triformal products

Examples 8 - 10

- 5 The surfactant concentration has a decisive influence on
the micellar two-phase hydroformylation, as the Examples
8 - 10 below show. For a micelle-aided hydroformylation
to be able to proceed, the critical micelle formation
concentration c.m.c. of the surfactant has to be main-
10 tained as a minimum concentration. Although a hydro-
formylation is possible in the premicellar region (0.85
times the c.m.c.), see Example 8, the reactivity
increases strongly with increasing surfactant concentra-
15 tion. The yields, particularly of triformal products,
increase and the yield becomes quantitative.

The results of a number of experiments using different
concentrations of the cationic surfactant tetradecyltri-
methylammonium bromide are summarized in Table 2. The
reaction conditions correspond to those of Example 1, but
20 the Rh concentration in the aqueous phase was 275 ppm by
weight. The volume ratio of catalyst phase to organic
phase was 3 : 1.

Table 2

		Surfactant conc. [mol/l]	Times c.m.c.	Conversion [% by wt.]	MF	DF	TF
	Ex. 8	0.018	0.85	55	32	19	11
25	Ex. 9	0.053	2.50	95	29	24	33
	Ex. 10	0.107	5.00	100	27	33	52

Sorry, there are no drawings for patent number 2162083.

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